Sintered foams obtained from different iron-rich waste

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Introduction

The synthesis of sintered glass ceramics and ceramic foams, obtained using three different waste precursors, is the topic under discussion. We propose investigations related to obtaining new inorganic foams from different waste raw materials, containing iron oxides. As a consequence, the observed sample expansion can be considered as an autocatalytic process, related to the oxygen release due to partial thermal reduction of Fe_2O_3.The studied materials are glass-ceramic foams (GCF), clinker waste brick foams (CWF) and new clay-brick foams (CYF).

Traditionally, the foaming process depends on the oxidation or decomposition reactions with the modifying compounds in glass-ceramic or ceramic bloating. Oxidation reactions usually are associated with the release of CO_2 gas from carbon-containing compounds like carbon black, graphite, silicon carbide (SiC) and organics reacting with the oxygen in the atmosphere. Typical decomposition reactions also are such with carbonates or sulfates leading to the release of CO_2 or SO_x respectively [1]. Interesting approach is the circumstance, when the batch contains intermediate oxides either iron oxides or manganese oxides undergoing transition from higher to lower oxidation state after reduction. In this case no addition of a foaming agent is required.

Materials and methods

The chemical compositions of used raw materials were evaluated by XRF Panalytical Zetium (USA). The phase compositions of final products were analyzed with XRD, Panalytical Emperean (USA). The thermal properties of the species were investigations by a thermal-optical measuring and imaging system ESS HSM-1400 ExpertLabService (Italy). HSM measurements are an established laboratory method in recent years, since it turns out to be reliable and fast and is used already by many research groups around the world [2-4].We investigate additionally the effect of the inert atmosphere, compared to atmospheric air to the foaming process. The structure was investigated by micro-computed tomography (μ-CT) Bruker SkyScan (Germany).

Results and discussion

The chemical compositions of the three studied materials are summarized in Table 1.

Table 1. Chemical composition by XRF.

Sample:	Composition [% wt.]:
GCF	SiO_2 49.2; Al_2O_3 5.1; Fe_2O_3 5.5; CaO 18.6; MgO 1.1; MnO 5.8; BaO 10.9; TiO_2 0.7; K_2O 0.7;
CWF	SiO_2 57.4±0.4; Al_2O_3 17.4±0.3; Fe_2O_3 8.4±0.2; CaO 1.1±0.1; MgO 2.6±0.1; BaO 1.2±0.1; TiO_2 5.2±0.2; K_2O 3.6±0.1; Na_2O 2.6±0.1;
CYF	SiO_2 52.394; Al_2O_3 25.21; Fe_2O_3 7.738; CaO 1.232; MgO 1.286; TiO_2 1.036; K_2O 1.613;

GCF is obtained by sintering of glass powder, arising from waste slag from the iron and steel company Helwan, Cairo Governorate, Egypt. It was enriched in SiO_2 by mixed 70 % wt. slag and 30 % wt. industrial sand. The batch was subsequently melted, quenched, sintered and exposed to thermal foaming. The HSM run is shown in Figure 1a. In this run after a linear heat treatment at 1050 ^oC in air environment starts intensive expansion of the volume leading to foam formation. The second run demonstrates that due to absence of oxygen, the reductive argon environment hinders the expansion maintained by oxygen release in the bulk of the partially amorphous foam. Thus instead of foam, a well densified material is being obtained. Figure 3a shows XRD pattern of corresponding glass-ceramics, obtained at 900^oC, with evident amorphous halo and moderate pyroxene amount below 40% [4].

The innovative point of current research is to use the partial Fe^{3+} reduction, starting at higher temperatures, toward the production of sintered glass-ceramic foam materials. As a result, samples with ~90 % closed porosity and fire resistance above 1000°C are obtained. In Figure 2a is shown 3-D reconstruction of the volume of such foam sample revealed by μ-CT scanning.

CWF is obtained after 1 h heat-treatment at 1250 ^oC of ceramic clinker culets. Since this temperature is higher than the production of clinkers, partial melting accompanied by Fe_2O_3 reduction is observed. As a result, similarly to GCF, foaming is taking place.

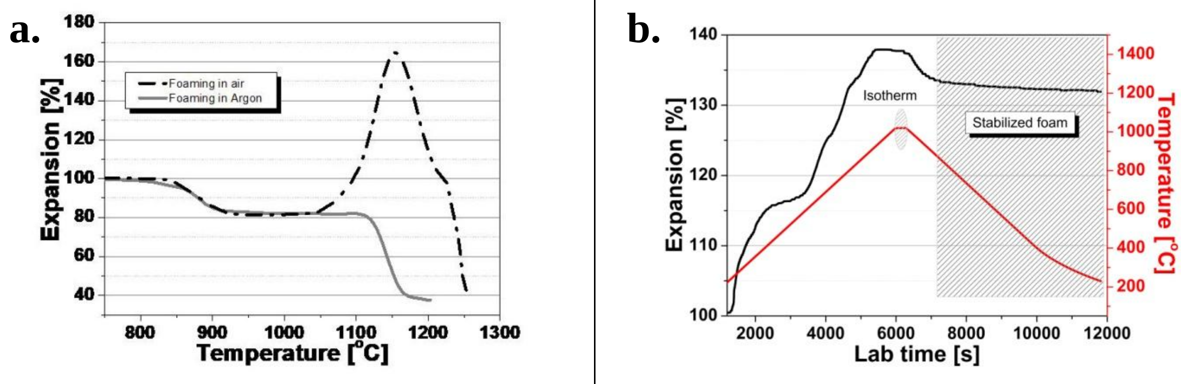

Figure 1. a. Typical HSM curves of the high-temperature behavior of pressed iron-rich glass-ceramic samples in air and Argon environment; **b.** Isothermal heat treatment of the synthesis of a glass-ceramic foam.

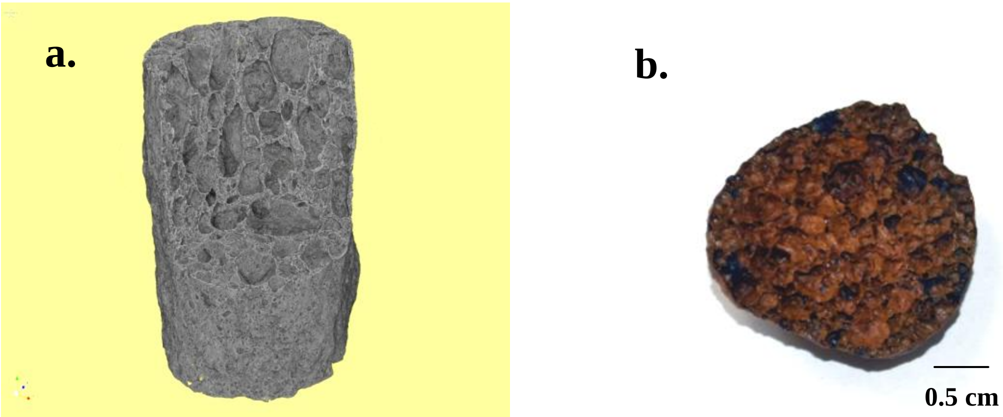

Figure 2. a. 3D-reconstruction of the volume of a foam sample;
b. A true-color image of a glass-ceramic foam sample: cross-section revealing the inner open pore population.

The corresponding XRD pattern is presented in Figure 3b. This result shows mainly an amorphous halo, somewhat similar to the one of GCF and residual quartz, together with traces of cordierite and pseudobrookite crystal phases. The crystallinity is reduced in comparison with that of the initial clinker, but sufficient to guarantee thermal stability up to 1200 ^{o}C. In Figure 2b is presented a true-color photograph of the newly obtained foam.

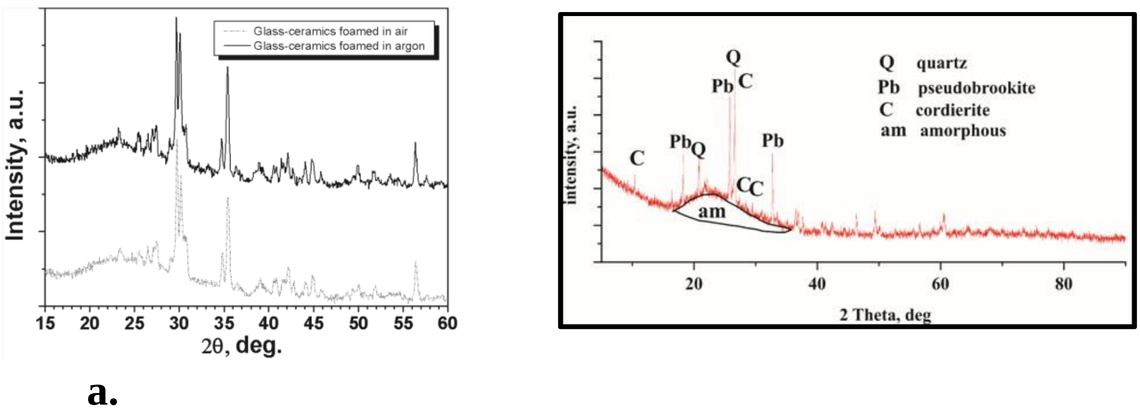

Figure 3. a.: XRD spectra of GCF glass-ceramics, obtained in air and argon; **b.**: XRD-pattern of the foamed sample CWF with revealed amorphous halo.

CYF is a waste clay from Maritza East mines, Bulgaria. It was mixed together with water glass in a ratio approx. 5:4 and then linearly heated at 10 $^{o}C\ min^{-1}$ up to 1020 ^{o}C with holding time of 15 min.

In Figure 1b is demonstrated the thermal *in-situ* synthesis of a fire-resistant foam in the HSM instrument. At cooling the newly synthesized foam is stable at more than 130 % expansion. It is interesting that the foaming behaviour is somewhat similar to GCF. The preliminary estimations show about 50 % closed porosity. Since the intensive foaming carries out at temperatures higher than those of clay's dehydration and/or decarbonisation of Na_2CO_3, a foaming mechanism related to F_2O_3 reduction might be considered as well.

Conclusions

Inorganic materials obtained by thermal foaming like these subjects of current investigation can be considered generally speaking as modern building materials, as low-cost construction materials and as insulation materials in various fields and industries, e.g., as panels or arbitrary shaped.

If properly engineered, the practice and experience show that a glassy-crystalline material with low density and high porosity of more than 85% can be obtained, which can be considered as more than a satisfactory result [1, 2]. Thus obtained foam is characterized by fire resistance features up to 1100°C as well.

In addition, interesting preliminary result with two new ceramics foam, also obtained due to high temperature Fe^{3+} reduction, are presented.

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